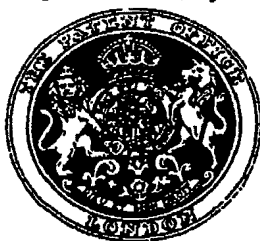


[Third Edition.]



## PATENT SPECIFICATION.

Application Date : May 19, 1943. No. 7941/43. 569,388

Complete Specification Left : Jan. 14, 1944.

Complete Specification Accepted : May 22, 1945.

### PROVISIONAL SPECIFICATION.

#### Improvements in or relating to the Formation of Adherent Silver Films on Non-Metallic Surfaces.

We, STANDARD TELEPHONES AND CABLES LIMITED, a British Company, ARCHIBALD ALAN NEW and EMRYS LLEWELLYN BODYCOMBE, both British Subjects, all of Connaught House, 68, Aldwych, London, W.C.2, do hereby declare the nature of this invention to be as follows :—

This invention relates to the formation of adherent silver films on non-metallic surfaces. It relates more particularly to the formation of a paste or suspension containing silver which is suitable for brushing, spraying or printing on non-metallic surfaces, by means of which tightly adherent silver films may be formed on non-metallic surfaces for decorative, mirror and electrical purposes. One of the main uses of the invention is the formation of electrodes of electrical condensers, such as silvered mica condensers.

Suspensions of the noble metals in various oils or resins have been known for a long time, but have the disadvantages that they must be fired at a high temperature of the order of 500—800° C. in order to burn off the last traces of the resinous binding materials, that they do not give a mirror finish by direct application, and that if used for electrical purposes they yield bad or capricious results when the power factors of the condensers are measured. In some cases the power factor of the condensers can be improved by after treatment, but this in itself is undesirable because it introduces additional processes.

We have found that in order to get good adhesion and mirror surfaces it is necessary to employ powders with a particle size less than 1 $\mu$  and, preferably averaging about 0.1 $\mu$ , and these when applied to mica or similar good dielectric give condensers of particularly good power factor.

According to one feature of the present invention a finely divided silver powder is produced by chemical precipitation in the presence of a protective colloid. The precipitate so formed (after washing) may then be formed into a paste suitable for brushing, printing or spraying with a liquid soluble in water to the extent to which it is used which can be completely boiled off below 850° C. such as glycerol, ethylene glycol, water or ethyl alcohol.

[Price 2/6.]

In a modification, instead of using a precipitate of silver to form the paste or suspension we use a precipitate of a silver salt which decomposes below 850° C., the other constituents of which are completely driven off by heat at or below that temperature. An example is silver formate.

In the use of chemical methods to attain the necessary small particle size, yielding a satisfactory film, certain general principles must be observed. The precipitation must take place from solutions of high concentration, the viscosity of the solutions must be high and the precipitated particles when formed must be peptised or stabilised. These last two requirements can be met by the addition of a small percentage of an organic compound of high molecular weight such as gelatine or liquorice extract. If silver is the precipitate, it must be formed at elevated temperatures.

Satisfactory results cannot be obtained by the use of residual iron as in the case of the well known Carey Lea type of colloidal silver. With this silver the adhesion obtained is not sufficiently high and when used for condensers the power factor is high. Moreover, it is not possible to prepare a dense enough paste from this silver to give really continuous films such as are necessary for electric condenser electrodes.

In order to maintain the small particle size and avoid any coagulation of the precipitate it is desirable to use a liquid vehicle for the paste which is mutually soluble with water to the extent to which it is used, and we have found water itself, glycerol, ethylene glycol, ethyl alcohol, and methyl alcohol to be suitable. The choice of liquid is governed by the speed of drying desired, this latter varying according to the process by which the paste or solution is to be applied, e.g. rapid drying is necessary in a spraying paste whereas comparatively slow drying is required in a printing paste.

#### EXAMPLE 1.

A solution (A) is prepared from:

Silver nitrate . . . . . 25 grams

Gelatine . . . . . 1 gram

Distilled water . . . . . 50 c.c.

The gelatine is swelled cold in a little

of the water first and the remainder added hot with stirring; the silver nitrate being then added in powder form and stirred till dissolved without further heating.

- 5 A second solution (B) of 15 grams of ammonium formate in 50 c.c. of distilled water is also prepared.

- 10 Solution A is placed in a large vessel (to allow for the frothing that takes place later) and is heated to  $90^{\circ}\text{C.} \pm 5^{\circ}\text{C.}$  Solution B is also heated to the same temperature and is then added to solution A with thorough mixing. A vigorous reaction takes place and silver nitrate is reduced to extremely finely divided metallic silver.

- 15 When the reaction is complete the silver is separated by centrifuging and the separated solid is washed by vigorous stirring in  $1\frac{1}{2}$  litres of distilled water. The silver is again separated by centrifuging. The washing process is repeated until a sample of the paste made up with the silver and one of the liquids mentioned above yields when applied to mica and burnt off at  $250^{\circ}\text{--}275^{\circ}\text{C.}$  an electrical condenser having a power factor lower than 0.0004 at 1 Kc.

- 20 A brushing or printing paste is prepared by adding pure glycerine to the wet silver powder, prepared as above, with vigorous stirring until the required consistency is obtained.

- 25 A spraying paste is obtained by adding to the wet silver powder with vigorous stirring, water, ethylene glycol, ethyl alcohol or methyl alcohol. A little glycerine may be added if desired. A spraying paste may also be obtained by adding water, methyl alcohol or ethyl alcohol to the brushing paste.

#### EXAMPLE 2.

- 45 Solution A:—  
Silver nitrate - - - 500 grams  
Gelatine - - - 27.5 grams  
Water (distilled) 1800 c.c.

- 50 The gelatine is swelled cold in a little of the water first, and the remainder added hot with stirring. The silver nitrate is added in powder form and stirred until dissolved without further heating.

The solution is poured into a 20 litre bowl and allowed to cool, when 300 grams of powdered solid ammonium formate are added with stirring until the resultant precipitate of silver formate is homogeneously dispersed in the liquid.

The bowl is then placed in a water bath at  $80^{\circ}\text{C.}$  and stirred until the reaction, which is violent, has ceased and silver is completely precipitated.

The silver is separated by means of a Sharples Super centrifuge at a speed of 25,000 r.p.m. until less than 1 gram of silver is left in the liquid. The silver contains excess gelatine and this is removed by agitating violently at  $60^{\circ}\text{--}80^{\circ}\text{C.}$  for some hours with distilled water.

The suspension is again centrifuged to obtain the purified silver. As it is difficult to control the above mentioned washing process so as to remove just the required excess of gelatine, the process is continued to remove more gelatine than is required to be removed. The wet silver is then made-up into a paste with the required vehicle and a little gelatine.

Pastes obtained as in either of the above examples, when brushed or sprayed on suitable laminations of mica which are then fired at  $250^{\circ}\text{--}300^{\circ}\text{C.}$  for 10 to 15 minutes, yield silvered mica condensers having power factors from 0.00005 to 0.0008 when measured at 1 Kc. per sec.

Although the invention has been described primarily for the purpose of silvered mica condensers, mirror surfaces may be formed on smooth transparent sheet material such as glass, quartz or mica by brushing, spraying or printing a paste prepared as above described on to the sheet and burning off at a temperature below  $350^{\circ}\text{C.}$  or even as low as  $250^{\circ}\text{C.}$  The mirror surface is seen through the base material.

Dated this 18th day of May, A.D. 1943.

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### COMPLETE SPECIFICATION

#### Improvements in or relating to the Formation of Adherent Silver Films on Non-Metallic Surfaces.

- 95 We, STANDARD TELEPHONES AND CABLES LIMITED, a British Company, ARCHIBALD ALAN NEW and EMYRS LIEWELLYN BODYCOMBE, both British Subjects, all of Connaught House, 68, Aldwych, London, W.C.2, England, do hereby declare the nature of this invention and in what man-

ner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to the formation of adherent silver films on non-metallic surfaces, to silver pastes suitable for use for that purpose and to the manufacture

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of finely comminuted silver suitable for incorporation in such paste. One of the main uses of the invention is the formation of electrodes of electrical condensers, such as silvered mica condensers.

Suspensions of the noble metals in various oils or resins have been known for a long time, but have the disadvantages that they must be fired at a high temperature of the order of 500-600° C. in order to burn off the last traces of the resinous binding materials, that they do not give a mirror finish by direct application, and that if used for electrical purposes they yield bad or capricious results when the power factors of the condensers are measured. In some cases the power factor of the condensers can be improved by after treatment, but this in itself is undesirable because it introduces additional processes.

It has been proposed to metallise fibrous materials by immersing them in a silver salt solution, precipitating silver from said solution on to the fibrous material by means of a reducing agent in the presence of colloidal substances and consolidating the precipitated metal to a lustrous coating by subjecting it to mechanical treatment. It has also been proposed to produce an electrode on the mica dielectric of an electrical condenser by applying to the mica a compound of silver such as silver oxide and a readily volatilisable reducing agent such as ammonium formate.

According to one feature of the present invention finely comminuted silver is manufactured by reacting together ammonium formate and a water solution of silver nitrate in the presence of a protective colloid.

We have found that in order to get good adhesion and mirror surfaces with a paste containing metallic silver it is necessary to employ powders with a particle size less than  $1\mu$ , and preferably averaging about  $0.1\mu$ , and these when applied to mica or similar good dielectric give condensers of particularly good power factor.

According to another feature of the invention, therefore, the manufacture of finely comminuted silver is carried out by precipitating silver from a solution of high concentration and high viscosity at an elevated temperature and peptising or stabilising the precipitated particles.

This may be carried out by making the precipitation from a solution of a silver salt of high concentration containing a dissolved organic compound of high molecular weight and stable at the precipitating temperature such as gelatine or liquorice extract.

Satisfactory results cannot be obtained by the use of residual iron as in the case of

the well known Carey Lea type of colloidal silver. With this silver the adhesion obtained when the silver is made into a paste and the paste is applied to a surface is not sufficiently high and when used for condensers the power factor is high. Moreover, it is not possible to prepare a dense enough paste from this silver to give really continuous films such as are necessary for electric condenser electrodes.

According to a further feature of the invention the manufacture of an adherent film of finely comminuted silver upon a non-metallic surface is carried out by precipitating silver in the presence of a protective colloid, mixing the precipitant with other constituents to form a paste, applying the paste to the said surface, and applying heat to drive off the non-silver constituents.

The precipitate (after washing) may be mixed into a paste suitable for brushing, printing or spraying. In order to maintain the small particle size and avoid any coagulation of the precipitate it is desirable to use a liquid vehicle for the paste which is mutually soluble with water to the extent to which it is used and we have found water itself, glycerol, ethylene glycol, ethyl alcohol, and methyl alcohol to be suitable. It is desirable, in order to obtain a uniform coating of good adhesion and free from foreign particles, that the liquid with which the washed silver is to be mixed should have a boiling point below 350° C. The choice of liquid is governed by the speed of drying desired, this latter varying according to the process by which the paste or solution is to be applied, e.g. rapid drying is necessary in a spraying paste whereas comparatively slow drying is required in a printing paste.

It may be necessary to add to the paste sufficient high molecular weight, water-soluble organic substance to bring the total percentage weight of such substances up to not more than 5% of the weight of paste.

#### EXAMPLE 1.

A solution (A) is prepared from:  
Silver nitrate . . . . 25 grams  
Gelatine . . . . . 1 gram  
Distilled water . . . . 50 c.c.

The gelatine is swelled cold in a little of the water first and the remainder added hot with stirring; the silver nitrate being then added in powder form and stirred till dissolved without further heating.

A second solution (B) of 15 grams of ammonium formate in 50 c.c. of distilled water is also prepared.

Solution A is placed in a large vessel (to allow for the frothing that takes place later) and is heated to 90° C.  $\pm$  5° C. Solu-

tion B is also heated to the same temperature and is then added to solution A with thorough mixing. A vigorous reaction takes place and silver nitrate is reduced to extremely finely divided metallic silver.

When the reaction is complete the silver is separated by centrifuging with a centrifuge whose separating force is at least 500 times that of gravity, and the separated solid is washed by vigorous stirring in  $1\frac{1}{2}$  litres of distilled water. The silver is again separated by centrifuging. The washing process is repeated until a sample of the paste is made up with the silver and one of the liquids mentioned above yields when applied to mica and burnt off at  $250^{\circ}$ — $275^{\circ}$  C. an electrical condenser having a power factor lower than 0.0004 at 1 Kc. per second.

A brushing or printing paste is prepared by adding pure glycerine to the wet silver powder, prepared as above, with vigorous stirring until the required consistency is obtained.

A spraying paste is obtained by adding to the wet silver powder, with vigorous stirring, water, ethylene glycol, ethyl alcohol or methyl alcohol. A little glycerine may be added if desired. A spraying paste may also be obtained by adding water, methyl alcohol or ethyl alcohol to the brushing paste.

#### EXAMPLE 2

##### Solution A:—

Silver nitrate	-	500	grams
Gelatine	- - -	27.5	grams
Water (distilled)		1800	c.c.

The gelatine is swelled cold in a little of the water first, and the remainder added hot with stirring. The silver nitrate is added in powder form and stirred until dissolved without further heating.

The solution is poured into a 20 litre bowl and allowed to cool, when 800 grams of powdered solid ammonium formate are added with stirring until the resultant precipitate of silver formate is homogeneously dispersed in the liquid.

The bowl is then placed in a water bath at  $80^{\circ}$  C. and stirred until the reaction, which is violent, has ceased and silver is completely precipitated. The temperature rises due to the reaction but should be kept at  $80^{\circ}$  C.— $100^{\circ}$  C., preferably  $85^{\circ}$  C.

The silver is separated by means of a Sharples Super centrifuge at a speed of 25,000 r.p.m. until less than 1 gram of silver is left in the liquid. The silver contains excess gelatine and this is removed by agitating violently at  $60^{\circ}$ — $80^{\circ}$  C. for some hours with distilled water.

The suspension is again centrifuged to obtain the purified silver. As it is difficult to control the above mentioned washing process so as to remove just the re-

quired excess of gelatine, the process is continued to remove more gelatine than is required to be removed. The wet silver is then made up into a paste with the required vehicle and a little gelatine.

Pastes obtained as in either of the above examples, when brushed or sprayed on suitable laminations of mica which are then fired at  $250^{\circ}$ — $300^{\circ}$  for 5 to 15 minutes (or even shorter times at higher temperatures up to  $350^{\circ}$  C., although the latter case needs critical control) yield silvered mica condensers having power factors from 0.00005 to 0.0008 when measured at 1 Kc. per second.

Although the invention has been described primarily for the purpose of silvered mica condensers, mirror surfaces may be formed on smooth transparent sheet material such as glass, quartz or mica by brushing, spraying or printing a paste prepared as above described on to the sheet and burning off at a temperature below  $350^{\circ}$  C. or even as low as  $250^{\circ}$  C. The mirror surface is seen through the base material.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. The manufacture of finely comminuted silver by reacting together ammonium formate and a water solution of silver nitrate in the presence of a protective colloid.

2. The manufacture of finely comminuted silver by reacting together water solutions of silver nitrate and ammonium formate in the presence of a protective colloid.

3. The manufacture of finely comminuted silver by precipitating silver from a solution of high concentration and high viscosity at an elevated temperature and peptising or stabilising the precipitated particles.

4. The manufacture as claimed in Claim 3 in which the precipitating of silver is from a solution of a silver salt of high concentration containing a dissolved organic compound of high molecular weight and stable at the precipitating temperature.

5. The manufacture of finely comminuted silver by mixing when cold powdered solid ammonium formate with a concentrated water solution of silver nitrate containing a little gelatine, and heating to a temperature of  $80^{\circ}$ — $100^{\circ}$  C., preferably about  $85^{\circ}$  C.

6. The manufacture of a silver paste for application to a surface by brushing, printing or spraying, comprising the manufacture of finely comminuted silver

as claimed in any of the preceding Claims and the mixing of said silver with a liquid mutually soluble with water to the extent to which it is used to form a paste.

- 5 7. The manufacture of a silver paste for application to a surface by brushing, printing or spraying, comprising the manufacture of finely comminuted silver as claimed in any of the Claims 1 to 5,  
10 separation of the said silver by repeated centrifuging with a centrifuge whose separating force is at least 500 times that of gravity and washing and finally mixing the separated silver with a liquid mutually  
15 soluble with water to the extent to which it is used, and adding, if necessary, sufficient gelatine or other high molecular weight water-soluble organic substance to bring the total percentage weight of such  
20 substance up to not more than 5% of the weight of paste.

8. The manufacture of an adherent film of silver upon a non-metallic surface which comprises precipitating silver in the man-  
25 ner claimed in any of the Claims 1 to 5, mixing into a paste with a liquid which is mutually soluble with the water in the precipitate applying the paste to the said surface and burning off.

- 30 9. The manufacture of an adherent film of finely comminuted silver upon a non-metallic surface by precipitating silver in the presence of a protective colloid, mixing the precipitant with other constituents  
35 to form a paste, applying said paste to the said surface, and applying heat to drive off the non-silver constituents.

10. The manufacture of an adherent film of silver upon a non-metallic surface  
40 by reducing a strong water solution of a silver salt whose viscosity has been substantially increased by the addition of a high-molecular weight water-soluble organic substance, washing the silver, so  
45 formed, incorporating the washed silver with a little of said organic substance in a sufficient quantity of liquid mutually

soluble with the water present having a boiling point below 350° C. to yield a paste or suspension suitable for applica-  
50 tion to said surface, applying said paste or suspension to said surface, and firing at a temperature below 350° C.

11. The manufacture as claimed in Claim 10 in which said silver salt is silver  
55 nitrate.

12. The manufacture as claimed in Claim 10 or 11 in which said organic sub-  
stance is gelatine.

13. The manufacture as claimed in Claim 10 or 11 in which said organic sub-  
60 stance is liquorice extract.

14. The manufacture as claimed in Claim 10, 11, 12 or 13, in which said  
65 liquid is water.

15. The manufacture as claimed in Claim 10, 11, 12 or 13 in which said liquid  
is glycerol.

16. The manufacture as claimed in Claim 10, 11, 12 or 13 in which said liquid  
70 is ethylene glycol.

17. The manufacture as claimed in Claim 10, 11, 12 or 13 in which said liquid  
is ethyl alcohol.

18. The manufacture as claimed in Claim 10, 11, 12 or 13 in which said liquid  
75 is methyl alcohol.

19. The manufacture as claimed in any of Claims 8 to 18 in which the surface  
80 is of mica.

20. The manufacture of an electrical condenser by use of the manufacture as  
claimed in any of Claims 8 to 19.

21. The manufacture of electrical condensers specifically as described in Ex-  
85 ample 1 or Example 2.

Dated this 14th day of January, A.D. 1944.

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